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PAPER

Spectroscopic and redox properties of amine-functionalized $K_2[Os^{II}(bpy)(CN)_4]$ complexes†

Michael J. Ahrens,*[a] Paul A. Bertin,[a] Adam G. Gaustad,[a] Dimitra Georganopoulou,[a] Markus Wunder,[a] Gary F. Blackburn,[a] Harry B. Gray[b] and Thomas J. Meade*[c]

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We report the first examples of amine-functionalized $K_2[Os^{II}(bpy)(CN)_4]$ (bpy = 2,2′-bipyridine) complexes. The tetracyanoosmate complexes were prepared by UV irradiation (λ = 254 nm) of $K_4[Os^{II}(CN)_6]$ and primary amine-functionalized bpy ligands in acidic aqueous media. The aqueous solution pH dependences of the spectroscopic and redox properties of 4,4′- and 5,5′-substituted complexes have been investigated. The pendant amine functional groups and coordinated cyanide ligands are basic sites that can be sequentially protonated, thereby allowing systematic tuning of electrochemical and optical spectroscopic properties.

Introduction

Transition metal complexes of the form $[M^{II}(NN)(CN)_4]^{2-}$ (where NN denotes a diimine ligand and M denotes Fe,[1] Ru,[2–5] or Os[6]) are of great interest, owing to their very rich photochemical, photophysical, and electrochemical properties, all exhibiting extraordinary sensitivity to solvation environment,[4,7,8] thus making them attractive candidates as probes for ligand-receptor interactions.[9]

Since the pioneering work of Olabe and coworkers,[6] relatively little attention has been paid to the $[Os^{II}(bpy)(CN)_4]^{2-}$ family of complexes.[10–12] These complexes absorb light throughout the visible region and are strong reductants in both ground and excited states. Additionally, since ligand photolabilization processes are disfavoured (Os^{II} d–d transitions are not excited in the visible region) and redox potentials can be readily tuned (using ligand substitution and/or changing solvent medium), they are prime candidates for investigations of charge and energy transport. Beyond coordination based constructs,[10] $[Os^{II}(bpy)(CN)_4]^{2-}$ complexes have not been incorporated into extended molecular systems. This can be largely attributed to a lack of synthetic methodology needed to produce functionalized complexes with verstaile synthetic "handles" suitable for further derivatization.

Herein, we report a novel method used to synthesize a series of $[Os^{II}(bpy)(CN)_4]^{2-}$ complexes that contain bpy ligands substituted with primary amine functional groups (**1**, **3**, **4**, **6**, Fig. 1). The spectral and electrochemical properties of these new derivatives can be tuned over a wide range by variations in pH in aqueous solutions.

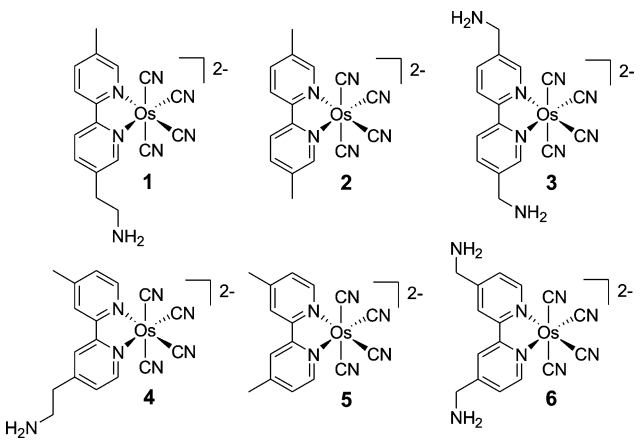


Fig. 1 $K_2[Os^{II}(bpy)(CN)_4]$ derivatives.

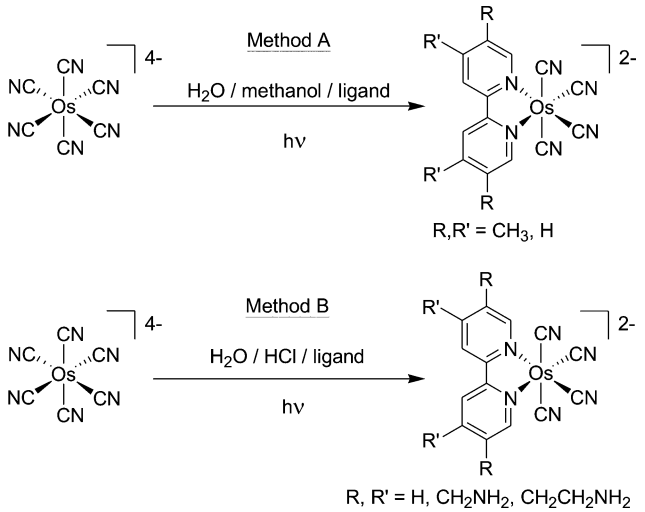
Results and discussion

Synthetic strategy

As first demonstrated by Posse *et al.*[6] and then by Baca *et al.*,[10] $[Os^{II}(bpy)(CN)_4]^{2-}$ complexes can be synthesized by photochemically activating $K_4[Os^{II}(CN)_6]$ in aqueous methanol containing the desired bpy ligand (Scheme 1, Method A). This method has been implemented successfully for both unsubstituted and 4,4′-^{t}Bu$_2$-bpy ligands in syntheses of the corresponding

[a]*Ohmx Corporation, 1801 Maple Avenue, Suite 6143, Evanston, Illinois, 60201, USA. E-mail: michael@ohmx.com; Fax: 1-847-491-8510*
[b]*Beckman Institute, California Institute of Technology, 1200 East California Blvd, MC 139-74, Pasadena, California, 91125, USA*
[c]*Departments of Chemistry, Biochemistry and Molecular and Cell Biology, Neurobiology and Physiology, and Radiology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA. E-mail: tmeade@northwestern.edu*

† Electronic supplementary information (ESI) available: Figure S1 (electronic spectra) and Figure S2 (cyclic voltammograms) for complexes **1–6** at three pH values. NMR spectra (^{1}H, ^{13}C, ^{13}C DEPT) and Table S1 reporting molar absorptivities for complexes **1–6**. See DOI: 10.1039/c0dt01478h



Scheme 1 Methods A and B used to prepare $K_2[Os^{II}(bpy)(CN)_4]$ complexes.

tetracyanoosmate (II) complexes. Application of this strategy with amine-functionalized bpy ligands to synthesize **1**, **3**, **4**, and **6** resulted in ligand decomposition without observable formation of tetracyanoosmate products. Employing acidic aqueous photochemical reaction conditions, we found that addition of HCl afforded the desired amine-functionalized tetracyanoosmate (II) complexes in reasonable yield (**1**, **3**, **4**, **6**, Fig. 1; Method B, Scheme 1). We assume that protonation of the -NH_2 functionality suppresses the decomposition pathway during photolysis by hindering charge transfer from the electron rich amines. It should be noted that alternate modifications of the synthetic protocol including the use of various aqueous/organic solvent mixtures, irradiation of aqueous $K_4[Os^{II}(CN)_6]$ followed by ligand addition post-photolysis, and high temperature ligand exchange in refluxing ethylene glycol all yielded trace amounts of the desired products that were heavily contaminated with inseparable side-products.

This new procedure (Method B, Scheme 1) allows for the introduction of pendant amine functional groups onto the bpy ligands prior to metallation, precluding the need to develop methods for derivatizing nonfunctionalized $[Os^{II}(bpy)(CN)_4]^{2-}$ complexes. The dimethyl-bipyridine complexes were synthesized in a similar manner using a mixture of water–methanol as the reaction media, excluding HCl (**2**, **5**, Fig. 1; Scheme 1, Method A). Our interest centers on monoamine and diamine bpy ligands, as they provide synthetic handles for further functionalization or serve as basic sites for pH-induced modification of complex properties. Both 4,4′ and 5,5′ analogues were investigated with the goal of determining the effect of ring substitution on spectroscopic and redox properties.

Electronic spectra of Os-bpy complexes

(a) General. The UV-vis absorption spectra of complexes **1–6** in aqueous solution at pH = 12.0 are shown in Fig. 2. The spectra have an absorption system in the 270–310 nm region that is attributable to intraligand (IL) π → π*(bpy) transitions. The broad feature in the 350–500 nm region can be assigned to ^{1}MLCT dπ(Os) → π*$_1$(bpy) with a weaker 500–600 nm ^{3}MLCT component. At higher energies within our observable window

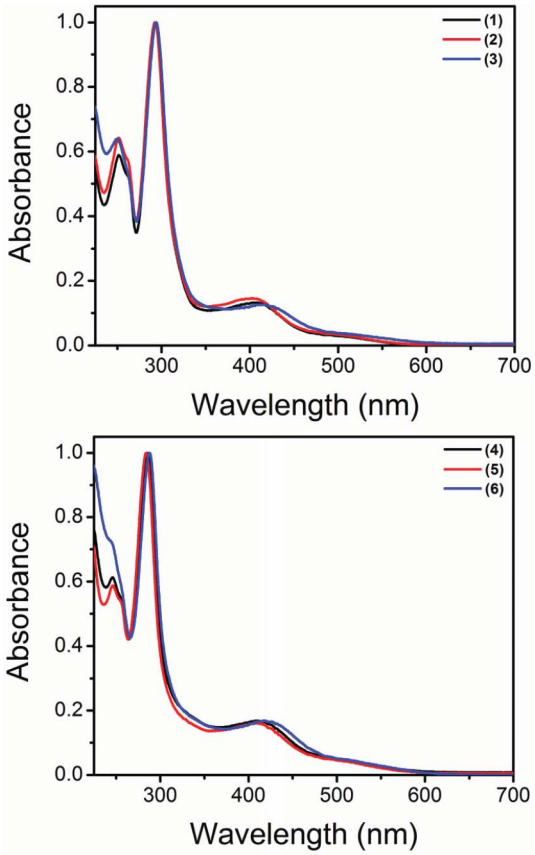


Fig. 2 Electronic spectra for complexes **1–6** in water at pH = 12.

are bands that most likely represent additional IL and dπ(Os) → π*(CN) transitions. Assignments of these bands for similar complexes have been discussed in previous reports.[6,10] Absorption spectra obtained at pH = 5.5 and pH = 1.5 (Figure S1) and molar absorptivity data (Table S1) are given in the Supplementary Information.†

(b) pH Effects. The electronic absorption spectrum of each complex was obtained in aqueous solution at three different pH values (1.5, 5.5, 12.0; see Figure S1† for spectral data). As summarized in Table 1, the ^{1}MLCT dπ(Os) → π*$_1$(bpy) features show a striking pH dependence. Complexes **2** and **5** have a single type of basic site (-CN), whereas **1**, **3**, **4**, and **6** have two types (-NH_2 and -CN). The pK_a values for these protonated ligands are ~ 2.2 and 9–10 for (-CNH^+)[6] and (-NH_3^+),[13] respectively, a difference that allows for sequential protonation of the ligands as

Table 1 Energies of dπ(Os) → π*$_1$(bpy) transitions as a function of aqueous solution pH

	E ($cm^{-1} \times 10^{-3}$)			ΔE ($cm^{-1} \times 10^{-3}$)
Complex	pH = 1.5	pH = 5.5	pH = 12	(1.5) – (12)
1	27.1	24.1	24.5	2.6
2	27.5	24.8	24.8	2.7
3	25.1	22.6	24.2	0.9
4	26.7	24.0	24.4	2.3
5	27.3	24.5	24.4	2.9
6	24.9	23.4	23.9	1.0

the pH is lowered from 12 (no protonation) to 5.5 (-NH_3^+) and finally to 1.5 (-NH_3^+, -CNH^+).

There is a pronounced effect on the dπ(Os) $\rightarrow$ π^*_1(bpy) transition energy for each complex, as will be discussed later (two different scenarios depending on the number and type of protonatable sites).

Complexes **2** and **5** with dimethyl-bpy ligands represent the simplest scenario where 2,700–2,800 cm^{-1} hypsochromic ^{1}MLCT shifts occur upon lowering the pH from 5.5 to 1.5. HOMO stabilization owing to π-electron density removal from the metal upon protonation of cyano ligands (-CNH^+) would increase the dπ(Os) $\rightarrow$ π^*_1(bpy) transition energy.[6]

Complexes **1**, **3**, **4**, and **6** present a more complex pH-dependent absorption scenario as both the -CN and -NH_2 sites on the complexes are protonatable. As described below, each of these processes has an opposite effect on the ^{1}MLCT energy. At pH = 12 both the -CN and -NH_2 exist in the free-base form, while at pH = 5.5 the -NH_2 becomes protonated to form -NH_3^+. Under these conditions, a bathochromic shift of the ^{1}MLCT transition on the order of 400–1500 cm^{-1} is observed depending on the complex. The influence of amine protonation on the complexes is two-fold: (1) withdrawal of electron density from the bpy ligand reduces the π-donating character and thus stabilizes the metal d orbitals through increased backbonding, and (2) marked stabilization of the bpy LUMO. The combined effects of these two processes produces an overall decreased energy for the dπ(Os) $\rightarrow$ π^*_1(bpy) transition, giving a net bathochromic shift for each complex at pH = 5.5.

Further decreasing the pH from 5.5 to 1.5 moves the ^{1}MLCT band to the highest energy measured, 900–2,600 cm^{-1} above that at pH 12 depending on the complex (see Table 1, last column). The two competing processes (-CNH^+ producing a hypsochromic shift and -NH_3^+ giving a bathochromic shift) are quite evident as comparisons are made across the series. The largest shifts belong to complexes **2** and **5** where there is no competing -NH_3^+-induced bathochromic shift (total hypsochromic shifts of 2,700 and 2,800 cm^{-1} respectively). Complexes **1** and **4** each contain a single pendant amine moiety, which upon protonation, induces a bathochromic shift (see discussion above). In addition, we would expect a lower pK_a value for the -CNH^+ ligands resultant from proximal protonated amines, thereby reducing the overall population of protonated species at pH = 1.5. Given the amine moieties are connected *via* an ethyl linkage (and the resultant electronic communication to the bpy π-system is weak) the effect on the -CNH^+ pK_a is expected to be minimal. This is reflected when comparing hypsochromic ^{1}MLCT band shifts from pH = 5.5 to pH = 1.5 for **1** and **4** (3,000 & 2,700 cm^{-1}) with **2** and **5** (2,700 & 2,800 cm^{-1}). Finally, for complexes **3** and **6** we observe the smallest hypsochromic shifts of 2,500 and 1,500 cm^{-1} respectively, going from pH = 5.5 to pH = 1.5. The reduced magnitude is primarily a result of a lowering of the pK_a for the -CNH^+ ligand. This effect is much more pronounced for **3** and **6** than **1** and **4** as there are two amines both linked *via* a methylene bridge enabling enhanced electronic communication with the bpy aromatic system. In all cases the metal-cyanide interaction is dominant in its effect on the electronic structures.

Cyclic voltammetry

(a) General. Complexes **1–6** were studied in aqueous solution using cyclic voltammetry to determine the half-wave potential ($E_{1/2}$; average of the oxidation and reduction potentials) and peak separation (ΔE_P; separation between anodic oxidation potential and cathodic reduction potential) values for the Os^{II}/Os^{III} redox couples.

Table 2 Electrochemical potentials for Os^{II}/Os^{III} redox couples

	$E_{1/2}$ (mV *vs.* SCE)			$\Delta E_{1/2}$ (mV)
Complex	pH = 1.5	pH = 5.5	pH = 12	(1.5 – 12)
1	492	453	419	73
2	464	411	410	54
3	541	528	434	107
4	476	430	407	69
5	445	392	395	50
6	524	507	421	103

(b) pH Effects. In a similar manner to the UV-vis spectroscopic studies, cyclic voltammograms were acquired at pH = 1.5, 5.5, and 12 to measure the effect of pH on the Os^{II}/Os^{III} redox couples (see Fig. 3, Table 2, and Figure S2). All complexes exhibited a one-electron oxidation with average ΔE_P values of 72 and 85 mV at lower pH (1.5 and 5.5) and 101 mV at elevated pH (12). These electrochemical values suggest "reversible" behavior at pH = 1.5 and 5.5 with some possible degradation processes at pH = 12. The model complexes **2** and **5** display no change in $E_{1/2}$ until -CN protonation at pH = 1.5. There is a moderate increase of 53 mV in the measured $E_{1/2}$ for complexes **2** and **5** going from pH = 5.5 to pH = 1.5 as -CNH^+ removes π-electron density from the metal, thereby disfavouring oxidation. Complexes **1** and **4** exhibit modest increases in $E_{1/2}$ going from pH = 12 to 5.5 (34 and 23 mV respectively) resulting from amine protonation. Further positive shifts of 39 and 46 mV are observed as the pH is lowered to 1.5. Complexes **3** and **6** display the largest $E_{1/2}$ increases (94 and 86 mV respectively) resulting from bpy ligand protonation at pH = 5.5, as there are two methylene-linked amine moieties. Further decreasing the pH to 1.5 results in minor increases in $E_{1/2}$ (13 and 17 mV respectively), providing additional evidence that the pK_a of the

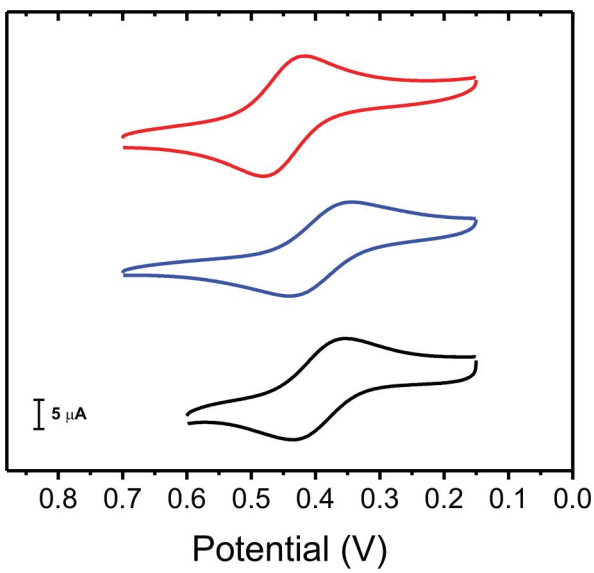


Fig. 3 Example cyclic voltammograms for (**5**) at pH = 1.5 (red), 5.5 (blue), and 12 (black) showing a 50 mV increase from pH = 12 to pH = 1.5.

-CNH^+ ligand is lowered as a result of the doubly-protonated bpy ligands.

Conclusions

We have demonstrated a novel synthetic method used to synthesize a series of amine-functionalized $K_2[Os^{II}(bpy)(CN)_4]$ complexes *via* photochemical activation of $K_4[Os^{II}(CN)_6]$ in acidic aqueous solutions. Investigations of the solution electrochemical behaviour of each complex have shown that the oxidation potentials of the Os^{II}/Os^{III} redox couples can be tuned by variations in pH. The observed values of the Os^{II}/Os^{III} potentials are well within the range required for electroactive self-assembled monolayer components,[14] and may be useful as alternative redox probes for use in our electrochemical biosensor program.[15,16] The new complexes we have characterized add greatly to members of the $[Os^{II}(NN)(CN)_4]^{2-}$ family and, most importantly, point the way for the design and construction of more highly tunable redox active centers.

Experimental

Materials

Organic 2,2′-bipyridine ligands were either purchased from Aldrich (4,4′-dimethyl-2,2′-bipyridine, 5,5′-dimethyl-2,2′-bipyridine), or synthesized according to literature procedures (4-aminoethyl-4′-methyl-2,2′-bipyridine,[17] 5-aminoethyl-5′-methyl-2,2′-bipyridine, 5,5′-diaminomethyl-2,2′-bipyridine,[18] 4,4′-diaminomethyl-2,2′-bipyridine).[19] $K_4[Os^{II}(CN)_6]$ was prepared as described previously,[20] and the ^{13}C NMR spectral information is provided herein since this data was lacking in the original report.

General procedures

All photochemical reactions were performed using a Rayonet RPR-200 photoreactor (Southern New England Ultraviolet Company; Branford, CT) equipped with 14 low-pressure Hg bulbs (λ = 254 nm). Reaction vessels were custom built quartz Schlenk tubes (0.9 cm i.d. × 32 cm long) obtained from Chemglass (Vineland, NJ). Water (18.2 MΩ × cm @ 25 °C) for reaction media and chromatography was taken from an Aqua Solutions (Jasper, GA) purification system and thoroughly deoxygenated with argon prior to use. Chromatography was carried out using Sephadex G-15 (60–80 μm; GE Healthcare) using an FPLC purification system (Pharmacia).

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 FT-NMR spectrometer (500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR, see Supplementary Information for spectra) and were processed with Bruker Topspin 2.1 software. ^1H NMR data are reported as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and peak assignments. ^{13}C NMR data are reported as chemical shift and multiplicity (based on ^{13}C DEPT data). ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS); ^{13}C chemical shifts are reported in ppm downfield from methanol.[21] Absorbance spectra were collected using an Ocean Optics S200 Dual Channel spectrometer equipped with a DH-2000-BAL light source. High resolution mass spectrometry (HRMS) was obtained on an Agilent 6210 LC-TOF mass spectrometer. Microanalyses were performed by Intertek (Whitehouse, NJ). Cyclic voltammetry measurements were performed using a CHI model 660A electrochemical analyzer (CH Instruments Inc.) with a standard single cell, three-electrode system equipped with platinum wire working[6,10,22–24] and counter electrodes (Bioanalytical Systems Inc.) and a SCE reference (CH Instruments Inc). All measurements were taken using millimolar aqueous solutions of the complexes at 25° C in 0.1 M KCl with a scan rate of 0.100 V s^{-1} and reported *versus* SCE.

General syntheses of $K_2[Os^{II}(bpy)(CN)_4]$ complexes

(a) where bpy contains one or more -NH_2 groups. Potassium hexacyanoosmate(II) (0.0571 g, 0.11 mmol) and 4-aminoethyl-4′-methyl-2,2′-bipyridine (0.0238 g, 0.11 mmol) were added to a 15 mL quartz Schlenk tube fitted with a magnetic stir bar. Water (10 mL) and 12 M hydrochloric acid (440 µL, 5.3 mmol) were added to the reaction flask and the contents deoxygenated by purging with argon for 25 min. The flask was sealed with a Teflon screwcap then irradiated in a Rayonet photoreactor (λ = 254 nm) for 15 h. The contents were transferred to a round bottom flask, the volatiles removed *in vacuo*, and the crude residue chromatographed on Sephadex G-15 (4 cm × 30 cm) using water as the eluent. The product was preceded by a mixture of unidentified side-products and eluted as the last colored band off the column. The desired product was obtained as a brown/red powder (0.0126 g, 0.02 mmol, 19.3%).

(b) where bpy contains only -CH_3 groups. Potassium hexacyanoosmate(II) (0.1102 g, 0.22 mmol) was added to a 100 mL Schlenk flask and dissolved in 20 mL water. 5,5′-Dimethyl-2,2′-bipyridine (0.0402 g, 0.22 mmol) was added to the flask, followed by 20 mL methanol. The contents were purged with argon for 20 min to deoxygenate the solution. During this time the bpy ligand dissolved to give a homogeneous solution. The contents were divided equally among 4 quartz Schlenk tubes of 15 mL capacity and each tube fitted with a magnetic stir bar. Each tube was further deoxygenated with argon for 2 min. The flasks were sealed with a Teflon screwcap then irradiated and purified in a similar manner as above. The desired product was obtained as a brown/red powder (0.0046 g, 0.01 mmol, 3.8%).

In all cases, the reported yields are *isolated yields* and are based on product obtained in ≥99% purity (see ^1H and ^{13}C NMR data in SI). Actual yields were much higher (30–50%) as there were frequently impure fractions remaining after column chromatography.

$K_4[Os^{II}(CN)_6]$ [20]

^{13}C NMR (D_2O): δ 143.3 (C). Anal. found: C, 14.32; H, 0.10; N, 16.54. Anal. calculated for $K_4[Os^{II}(CN)_6]$: C, 14.33; H, 0; N, 16.72.

$K_2[Os^{II}(CN)_4$-5-aminoethyl-5′-methyl-2,2′-bipyridine] (1)

^1H NMR (D_2O): δ 2.39 (s, 3H, -C*H*$_3$), 3.08 (t, J = 7.26 Hz, 2H, -C*H*$_2$), 3.34 (t, J = 7.26 Hz, 2H, -C*H*$_2$), 7.62, (d, J = 8.03 Hz, 1H, aromatic-*H*), 7.71 (d, J = 8.03 Hz, 1H, aromatic-*H*), 7.96 (d, J = 8.02 Hz, 1H, aromatic-*H*), 8.02 (d, J = 8.02 Hz, 1H, aromatic-*H*), 9.12 (s, 1H, aromatic-*H*), 9.18 (s, 1H, aromatic-*H*). $^{13}C\{^1H\}$ NMR (D_2O): δ 18.0 (CH_3), 30.2 (CH_2), 40.5 (CH_2), 123.0 (CH),

123.1 (CH), 135.9 (C), 137.5 (CH), 137.8 (CH), 138.4 (C), 146.0 (C), 146.5 (C), 149.7 (C), 153.2 (CH), 153.5 (CH), 154.9 (C), 157.3 (C). HRMS calculated for $C_{17}H_{15}N_7Os$ (M^-): 509.1004. HRMS observed: 509.1003. 0.0065 g, 0.011 mmol, 9.6%.

$K_2[Os^{II}(CN)_4$-5,5′-dimethyl-2,2′-bipyridine] (2)

^1H NMR (D_2O): δ 2.39 (s, 6H, -CH_3), 7.53 (d, J = 7.74 Hz, 2H, aromatic-H), 7.85, (d, J = 8.24 Hz, 2H, aromatic-H), 9.09 (s, 2H, aromatic-H). $^{13}C\{^1H\}$ NMR (D_2O): δ 18.0 (CH_3), 122.5 (CH), 137.6 (CH), 137.7 (C), 146.9 (C), 150.1 (C), 153.3 (CH), 155.3 (C). HRMS calculated for $C_{16}H_{12}N_6Os$ (M^-): 480.0738. HRMS observed: 480.0736. 0.0046 g, 0.008 mmol, 3.8%.

$K_2[Os^{II}(CN)_4$-5,5′-bis(aminomethyl)-2,2′-bipyridine] (3)

^1H NMR (D_2O): δ 4.09 (s, 4H, NH_2–CH_2), 7.89 (m, 2H, aromatic-H), 8.20 (m, 2H, aromatic-H), 9.29 (s, 2H, aromatic-H). $^{13}C\{^1H\}$ NMR (D_2O): δ 41.5 (CH_2), 123.7 (CH), 136.9 (CH), 137.5 (C), 145.5 (C), 149.2 (C), 152.9 (CH), 157.2 (C). HRMS calculated for $C_{16}H_{15}N_8Os$ $(M+H)^-$: 511.1035. HRMS observed: 511.1021. 0.0365 g, 0.062 mmol, 28.4%.

$K_2[Os^{II}(CN)_4$-4-aminoethyl-4′-methyl-2,2′-bipyridine] (4)

^1H NMR (D_2O): δ 2.35 (s, 3H, -CH_3), 3.02 (t, 2H, J = 7.38 Hz, CH_2), 3.27 (t, 2H, J = 7.38 Hz, CH_2), 7.24 (d, J = 7.66 Hz, 1H, aromatic-H), 7.27 (d, J = 7.66 Hz, 1H, aromatic-H), 7.91 (s, 1H), 8.00 (s, 1H), 9.05 (d, J = 5.72 Hz, 1H, aromatic-H), 9.16 (d, J = 5.72 Hz, 1H, aromatic-H). $^{13}C\{^1H\}$ NMR (D_2O): δ 21.1 (CH_3), 32.8 (CH_2), 40.0 (CH_2), 123.6 (CH), 124.4 (CH), 127.7 (CH), 128.6 (CH), 146.2 (C), 146.4 (C), 147.0 (C), 149.6 (C), 149.8 (C), 152.6 (CH), 153.2 (CH), 157.2, (C), 158.5 (C). HRMS calculated for $C_{17}H_{15}N_7Os$ (M^-): 509.1004. HRMS observed: 509.1014. 0.0126 g, 0.022 mmol, 19.3%.

$K_2[Os^{II}(CN)_4$-4,4′-dimethyl-2,2′-bipyridine] (5)

^1H NMR (D_2O): δ 2.37 (s, 6H, -CH_3), 7.22 (m, 2H, aromatic-H), 7.92 (m, 2H, aromatic-H), 9.04 (d, J = 5.64 Hz, 2H, aromatic-H). $^{13}C\{^1H\}$ NMR (D_2O): δ 21.2 (CH_3), 124.0 (CH), 128.3 (CH), 147.1 (C), 149.4 (C), 150.2 (C), 152.4 (CH), 157.5(C). HRMS calculated for $C_{16}H_{12}N_6Os$ (M^-): 480.0738. HRMS observed: 480.0740. 0.0244 g, 0.044 mmol, 21.7%.

$K_2[Os^{II}(CN)_4$-4,4′-bis(aminomethyl)-2,2′-bipyridine] (6)

^1H NMR (D_2O): δ 4.11 (s, 4H, NH_2–CH_2), 7.42 (d, J = 5.74 Hz, 2H, aromatic-H), 8.21 (s, 2H, aromatic-H), 9.24 (d, J = 5.74 Hz, 2H, aromatic-H). $^{13}C\{^1H\}$ NMR (D_2O): δ 43.2 (CH_2), 122.9 (CH), 126.6 (CH), 143.7 (C), 145.3 (C), 149.3 (C), 153.5 (CH), 158.2 (C). HRMS calculated for $C_{16}H_{14}N_8Os$ (M^-): 510.0956. HRMS observed: 510.0952. 0.0207 g, 0.035 mmol, 26.8%.

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